Remarks

The present invention relates to a radiation patternable functional material, comprising nanoparticles of an electronically functional substance selected from the group consisting of semiconductors and metals, and a plurality of ligands bound to each of the nanoparticles. The ligands contain a photoreactive group or a group that is reactive with a photochemically generated species and that, after first-order photoreaction or reacting with the photochemically generated species, materially changes the solubility characteristics of the material in a developer. After irradiation, developing and curing, the present radiation patternable functional material forms a patterned film of an electronically conducting or semiconducting material.

The reference cited against the claims (Hanabata et al., U.S. Pat. No. 6,921,623 [hereinafter "Hanabata et al."] neither discloses nor suggests a radiation patternable functional material that forms a patterned film of an electronically conducting or semiconducting material (see amended Claim 1 above). Furthermore, Hanabata et al. do not appear to enable one to make a radiation patternable functional material comprising nanoparticles of an electronically functional substance selected from the group consisting of semiconductors and metals (see amended Claim 1), having ligands bound thereto that can change the solubility characteristics of the material in a developer. Consequently, the present claims are patentable over the cited reference.

The Rejection of Claims 1-20 under 35 U.S.C. § 102(e)

The rejection of Claims 1-20 under 35 U.S.C. § 102(e) as being anticipated by Hanabata et al. is respectfully traversed.

Hanabata et al. discloses a photosensitive resin composition comprising an active component selected from an active metal alkoxide represented by the formula (1) or a polycondensate thereof and a particle represented by the formula (2):

$$(X)_{m-n}\text{-}M^{m}\text{-}[(U_1)_p\text{—}(U_2\text{-}Z)_t]_n \qquad (1)$$

$$P\text{—}[(Y)_s\text{—}\{(U_1)_p\text{—}(U_2\text{-}Z)_t\}]_k \qquad (2)$$

wherein X (presumably) is a hydrogen, a halogen, an alkoxy group or an alkoxycarbonyl group, M (presumably) is a metal atom whose valence m is not less than 2, U_1 (presumably) is a first connecting unit, U^2 (presumably) is a second connecting unit and Z (presumably) is a group causing a difference in solubility by light exposure, P (presumably) is a fine particle carrier, Y (presumably) is a coupling residue, n (presumably) is an integer of not less than 1, m > n, p (presumably) is 0 or 1, t (presumably) is 1 or 2, k (presumably) is an integer of not less than 1, and s (presumably) is 0 or 1 (Abstract, ll. 1-16).

This material is intended as a high-resolution photoresist material, not as an electronically conducting or semiconducting material. For example, Hanabata et al. teach that in the field of semiconductor integrated circuit resists, light sources of shorter wavelength such as KrF, ArF and F_2 excimer lasers are used instead of conventional g-ray or i-ray high-pressure mercury lamps (col. 1, ll. 21-28). However, when a KrF or ArF excimer laser is applied to a conventional resist material such as a novolak resin/diazonaphthoquinone-based positive resist, sensitivity and resolution of the conventional resist materials deteriorate due to light absorption by the novolak resin (col. 1, ll. 29-34).

Moreover, with increases in the integration level and performance of semiconductor integrated circuits, there has been demand for resists with better resolution and for etching resistance improvement in dry development (col. 1, ll. 35-40). Thus, in one prior approach, inorganic fine particles, such as silicasol, have been used to impart both resist performance (sensitivity, improved resolution, etc.) and dry etching resistance to a photosensitive resin (col. 1, ll. 41-47). The literature discloses that a resist system using a transparent SiO_2 nanoparticle is useful to wavelengths such as 157 nm (col. 2, ll. 5-7).

Hanabata et al. found that the combination of an active component and a photosensitive resin composition can form a high resolution pattern with high sensitivity when a functional group is introduced into the active component. For example, a fine or finely divided particle (an

active particle) can become hydrophilic by eliminating a hydrophobic leaving group upon light exposure, and the active component can be a specific metal alkoxide (an active metal alkoxide) or the polycondensate thereof (an active particle formed by polycondensation). Thus, light exposure can cause a difference in solubility, and the combination of the metal alkoxide or a polycondensate thereof, and a photosensitive resin composition, may form a high(er) resolution pattern with higher sensitivity because of a reduction of impurity incorporation (col. 3, ll. 13-32).

The invention of Hanabata et al. includes a photosensitive resin composition which comprises a base resin, a photosensitizer and the active component (col. 5, ll. 45-48). To form a pattern, the photosensitive composition may be applied or coated onto a substrate, the coating layer may be exposed to light, the light-exposed layer may be heat-treated, and the heat-treated layer may be developed (col. 5, ll. 54-58 of Hanabata et al.).

The active component (or ingredient) of the present invention is used (or usable) in combination with a photosensitizer which constitutes a photosensitive resin composition, and has a unit for causing a difference in solubility owing to at least light exposure (col. 6, ll. 27-31). Such an active component comprises at least one member selected from the group consisting of the active metal alkoxide represented by the formula (1) above or the polycondensate thereof, and the particle represented by the formula (2) above (col. 6, ll. 31-35). Although many possible metals are contemplated, Hanabata et al. teach that the metal atom M may be aluminum, titanium, zirconium or silicon, and (consistent with the teachings relating to the prior photoresist approach discussed above) ***is usually silicon*** (col. 4, ll. 33-34; emphasis added). Thus, it appears that <u>Hanabata et al. simply intend their photosensitive composition to form a patternable resist material, rather than a patterned electronically conducting or semiconducting material</u>.

Hanabata further teach the importance of a transparent particle. For example, when the mean particle size of the active particle is smaller than an exposing wavelength, ***because the active particle is substantially transparent to the exposing wavelength***, light exposure can be conducted to the depth of the photosensitive layer even if the layer is thickened (col. 15, ll. 56-60; emphasis added). As a result, sensitivity and resolution can be improved as much as a

pattern with high sensitivity and high resolution can be formed in regard to a light source of shorter wavelength (col. 15, ll. 60-63).

The use of UV-absorbent metal nanoparticles (see, e.g., amended claim 3 above) may be detrimental to the suggested advantages of the invention of Hanabata et al. While it is generally understood in the art that nanoparticles having a size less than 100 nm do not scatter light (assuming they are not agglomerated in larger secondary particles), many metal nanoparticles (in particular gold, silver, and copper) have some strong characteristic UV absorptions. These absorptions are expected to reduce the sensitivity of the resist of Hanabata et al., and limit its usefulness for high resolution patterning.

Furthermore, when their composition contains a particle or polycondensate, Hanabata et al. do not appear to enable one to make a patternable material comprising semiconductor and/or metal nanoparticles having ligands bound thereto that can change the solubility characteristics of the material in a developer and that, after irradiation, developing and curing, can form a patterned film of an electronically conducting or semiconducting material. For example, the polycondensate of Hanabata et al. may be a polycondensate of the active metal alkoxide represented by the formula (1) alone (singly) or a polycondensate (copolycondensate) of the active metal alkoxide represented by the formula (1) and a metal alkoxide represented by the following formula (5):

$$(X)_{m-n-1}M^{m}(R^5)_{n-1} \quad (5)$$

wherein R^5 represents a hydrogen atom or an alkyl group, X, M, m and n have the same meanings defined above (col. 4, l. 65-col. 5, l. 8). The polycondensate of Hanabata et al. appears to be an active particle formed by polycondensation (col. 3, ll. 23-26).

Thus, Hanabata et al. discloses an oligomer or an active particle, which comprises at least a polycondensate of the active metal alkoxide. An active component (especially an active particle) as disclosed by Hanabata et al. may comprise a polycondensate of the above-mentioned active metal alkoxide. Such an active component may be an active particle in the form of a particulate (particulate matter), or a liquid or solid oligomer. The active component [or?] the

polycondensate of the active component can be obtained by polycondensing the active metal alkoxide by a conventional sol-gel method to form of a polymer or a sol (col. 14, ll. 44-53).

As is known in the art, polycondensation (or polymerization) of metal alkoxides by the sol-gel method leads to formation of **metal oxides**. For example, an electronic search of the USPTO patent full-text database for all patents including the terms ***sol, gel, oxide, metal*** and ***alkoxide*** in the claims yielded 92 such patents. A cursory review of a sample of these patents showed that application of the sol-gel method to a metal alkoxide leads to formation of metal oxides, and not the corresponding metal. Therefore, any material or compound based on the metal alkoxide polycondensate of Hanabata et al. does not anticipate the presently claimed composition containing nanoparticles of a metal or a composition that, after irradiation, developing and curing, forms a patterned film of an electronically conducting or semiconducting material.

However, the particle P of Hanabata et al. (see formula (2) above) may be an organic fine particle carrier or an inorganic fine particle carrier (e.g., silicasol; see, e.g., col. 3, ll. 51-56, and col. 5, ll. 17-19; see also col. 17, l. 51-col. 18, l. 14). In this latter passage, Hanabata et al. disclose a number of inorganic fine particle carriers, including a metal alone (simple or single metal; e.g., gold, silver, copper, platinum, aluminum), an inorganic oxide (e.g., silica [e.g., silica sol such as colloidal silica, aerogels, glass], alumina, titania, zirconia, zinc oxide, copper oxide, lead oxide, yttrium oxide, tin oxide, indium oxide, magnesium oxide), an inorganic carbonate (e.g., calcium carbonate and magnesium carbonate), an inorganic sulfate (e.g., barium sulfate and calcium sulfate), a phosphate (e.g., calcium phosphate and magnesium phosphate), and the like, which include sols and gels prepared by, for example, a sol-gel method, and which can be used either singly or in combination. ***However, Hanabata et al. only discloses and enables inorganic particles having hydroxide*** (or, perhaps, some combination of hydroxide and oxide) ***groups on the surface for linking to a coupling agent residue Y***.

For example, Hanabata et al. teach that a hydrophilic group is introduced into an inorganic fine particle through both a coupling agent and a connecting unit (col. 16, ll. 63-65). Each component may be bonded by reacting a connecting unit U having two hydroxyl groups

with a coupling agent Y having an isocyanate group (e.g., a silane coupling agent) to form a compound having a free hydroxyl group and a coupling group (an alkoxy group or a halogen atom), wherein the coupling agent is bonded to one of hydroxyl groups of the unit; protecting the free hydroxyl group by a protective group such as t-BOC group; and then reacting an inorganic fine particle carrier (e.g., silicasol, etc.) with the coupling group (the alkoxy group or the halogen atom; see col. 16, l. 65-col. 17, l. 9). Other processes may be employed, but they also appear to bind the hydrophilic group-containing compound with an inorganic fine particle carrier via the alkoxy group or halogen atom site in the (silane) coupling agent (see, e.g., col. 17, ll. 10-30 of Hanabata et al.). Thus, Hanabata et al. appear to teach that an alkoxy group or halogen atom in the coupling agent is required for introducing the hydrophilic group (i.e., the group giving the composition its photosensitive properties; see, e.g., col. 3, l. 66-col. 4, l. 17) into an inorganic fine particle.

Specifically with regard to the inorganic particle, Hanabata et al. disclose examples of coupling agents (corresponding to a residue Y in formula (2) above) including an organic metal compound containing an alkaline earth metal, a transition metal, a rare earth metal, or a metal element of the Groups 3 to 5 and 13 to 15 of the Periodic Table of Elements, especially a metal element of the Groups 4, 13 and 14 of the Periodic Table of Elements, for example, aluminum, titanium, zirconium, and silicon. Among the organic metal compounds, a titanium coupling agent and a silane coupling agent (especially the silane coupling agent) are preferred (col. 18, l. 41-51).

The silane coupling agent includes the coupling agents represented by the formula (4):

$$(R^5)_u Si(D)_{4-w} \qquad (4)$$

The reactive group D corresponding to the fine particle carrier of the coupling agent (4) is usually a halogen atom (bromine atom, chlorine atom, etc.), ***or a hydrolytic condensable group*** such as an alkoxy group (e.g., a C_{1-4} alkoxy group such as methoxy group and ethoxy group; see col. 18, l. 52-59 of Hanabata et al.; emphasis added). As is known in the art, many metal halides such as $TiCl_4$ and $SiCl_4$ are reactive towards oxygen-containing compounds (see, e.g., Cotton et al., "Advanced Inorganic Chemistry," John Wiley & Sons, New York (1999), pp. 271-272, 282-

285, 472-474, and 558-559), and the hydrolytic condensable groups of Hanabata et al. result in the formation of metal-**oxygen**-silicon bonds, typically from a hydroxy group on the metal.

Thus, the silane coupling agents disclosed by Hanabata et al. are known to be reactive with the oxygen-containing species, such as oxo or hydroxy groups (which are bound directly to a metal; i.e., metal oxides and/or hydroxides). On the other hand, it is not expected (and the evidence of record does not show) that the silane coupling agents disclosed by Hanabata et al. would be reactive with metal or semiconductor particles not having oxygen-containing species on the surface. For example, it is believed that the disclosure of Hanabata et al. does not enable coupling of a silane coupling agent to metal particles which are generally considered not to form oxide surfaces (e.g., gold, silver and platinum). Instead, an attempt to couple their silane coupling agent to such metal particles under state of the art coupling conditions would be likely to crosslink the silane coupling agent, rather than couple it to the metal nanoparticle. Thus, the "simple or single" metal particle of Hanabata et al. appears to be one that contains hydroxide and/or oxide groups on its surface, consistent with the remainder of their disclosure.

The organic metal compounds of Hanabata et al. containing, as the metal M, aluminum, titanium or zirconium, may be exemplified by the organic metal compounds corresponding to the above-mentioned silane coupling agents (col. 19, ll. 3-7). Thus, the possibility of other metals being used in the coupling agent of Hanabata et al. does not cure any deficiency of Hanabata et al. with regard to disclosing or enabling a radiation patternable functional material comprising nanoparticles of an electronically functional substance selected from the group consisting of semiconductors and metals, and a plurality of ligands bound to each of the nanoparticles.

Therefore, Hanabata et al. neither discloses nor suggests a radiation patternable functional material comprising nanoparticles of an electronically functional substance selected from the group consisting of semiconductors and metals, having ligands bound thereto that can change the solubility characteristics of the material in a developer and that forms a patterned film of an electronically conducting or semiconducting material (see amended Claim 1 above). Furthermore, Hanabata et al. do not appear to enable one skilled in the art to make such a material. Consequently, this ground of rejection is unsustainable, and should be withdrawn.

Election/Restriction

As set forth in the Restriction Response filed May 19, 2005, the restriction requirement was traversed on a number of bases:

- The relationship between various groups has been mischaracterized (e.g., Groups I and II, Groups I and III, Groups I and IV, Groups I and V, Groups I and VI, Groups II and III, Groups II and IV, Groups II and VI, Groups III and IV, Groups III and V, Groups IV and V, Groups IV and VI, Groups V and VI);
- The reasons and/or examples in support of the conclusions of unrelatedness are technically and factually inaccurate, and/or logically and legally inadequate (e.g., Groups I and II, Groups I and III, Groups I and IV, Groups I and V, Groups I and VI, Groups II and III, Groups II and IV, Groups II and V, Groups II and VI, Groups III and IV, Groups III and V, Groups III and VI, Groups IV and V, Groups IV and VI, Groups V and VI);
- Limitations common to claims in both groups appear to have been overlooked (e.g., Groups I and II, Groups II and III, Groups III and IV, Groups IV and VI);
- One of the groups includes claims that depend from a claim in the other group (e.g., Groups I and III, Groups I and IV, Groups I and V, Groups I and VI, Groups II and V);
- At least one reason and/or example in support of restriction bears no relation to restriction between the identified groups, and appears to be somewhat nonsensical (Groups II and IV);
- No adequate reason or actual example to support restriction between the groups has been provided (Groups II and V, Groups III and VI); and/or

- The premise of unrelatedness has been restated as the reason and/or example supporting the conclusion for finding the same Groups I and V, Groups IV and V, Groups IV and VI, Groups V and VI).

Applicants have now amended the claims so that every pending claim depends, directly or indirectly, from Claim 1. Simply put, it is not proper to restrict between a dependent claim and the independent claim from which it depends. Otherwise, the USPTO could limit every patent to a single claim; a claim would be patentable merely because its scope differed from other claims; and the concept of obviousness would simply not exist. Applicants are also concurrently filing a Petition to Withdraw the Restriction Requirement, a courtesy copy of which is attached hereto for the Examiner's convenience.

Early notice of the withdrawal of the restriction requirement is earnestly requested.

Conclusions

In view of the above amendments and remarks, all bases for objection and rejection are believed to be overcome, and the application is believed to be in condition for allowance. Early notice to that effect is earnestly requested.

If it is deemed helpful or beneficial to the efficient prosecution of the present application, the Examiner is invited to contact Applicant's undersigned representative by telephone.

Respectfully submitted,

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Library of Congress Cataloging in Publication Data:

Advanced inorganic chemistry. --6th ed. / by F. Albert Cotton, Geoffrey Wilkinson, Carlos A. Murillo, and Manfred Bochmann; with a chapter on boron by Russell Grimes.
p. cm.
Prev. ed. entered under Cotton.
"A Wiley-Interscience publication."
Includes index.
ISBN 0-471-19957-5 (alk. paper)
1. Chemistry, Inorganic. I. Cotton, F. Albert (Frank Albert), 1930- . II. Wilkinson, Geoffrey. III. Murillo, Carlos A., IV. Bochmann, Manfred. IV. Grimes, Russell N.
GD151.2.C68 1999
546--dc21

98-8020

Printed in the United States of America.

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Fluorides

These are obtained by fluorination of the other halides or by direct interaction; GeF_4 is best made by heating $BaGeF_6$. Tetrafluorides of Si and Ge are hydrolyzed by an excess of water to the hydrous oxides; the main product from SiF_4 and H_2O in the gas phase is $F_3SiOSiF_3$. In an excess of aqueous HF, the hexafluoro anions (MF_6^{2-}) are formed. These anions are also found with certain trivalent cations, e.g., $SmSnF_7$ and $TlPbF_7$.[31] Similarly, a solid state reaction of tin metal and $(NH_4)HF_2$ gives:

$$2Sn + 7(NH_4)HF_2 \xrightarrow{300°C} 2(NH_4)_3SnF_7 + 4H_2 + NH_3$$

In these EF_7^{3-} species the stiochiometry might be misleading in regard to their structure because they all contain $[SnF_6]^{2-}$ octahedra and F^- anions surrounded by the corresponding cations.[32] Germanium tetrafluoride can be reduced to give hygroscopic mixed-valent species such as Ge_5F_{12} and Ge_7F_{16}.[33] Tin tetrafluoride is polymeric, with Sn octahedrally coordinated by four bridging and two nonbridging F atoms. Non-stoichiometric lead tetrafluoride is made by the action of F_2 on PbF_2, but the pure material can be prepared by high-pressure fluorination of "PbF_{4-x}"; it is isostructural with SnF_4.[34]

Silicon Halides

Silicon tetrachloride is made by chlorination of Si at red heat. Hexachlorodisilane (Si_2Cl_6) can be obtained by interaction of $SiCl_4$ and Si at high temperatures or, along with $SiCl_4$ and higher chlorides, by chlorination of a silicide such as that of calcium. The higher members, which have highly branched structures, can also be obtained by amine-catalyzed reactions such as

$$5Si_2Cl_6 \longrightarrow Si_6Cl_{14} + 4SiCl_4$$

$$3Si_3Cl_8 \longrightarrow Si_5Cl_{12} + 2Si_2Cl_6$$

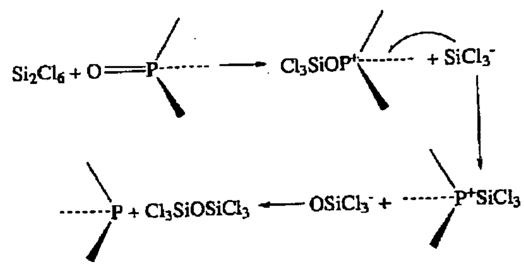
and by photolysis of $SiHCl_3$. The products are separated by fractional distillation.

All the chlorides are immediately and completely hydrolyzed by water, but careful hydrolysis of $SiCl_4$ gives $Cl_3SiOSiCl_3$ and $(Cl_3SiO)_2SiCl_2$.

Hexachlorodisilane is a useful reducing agent for compounds with oxygen bound to S, N, or P; under mild conditions, at 25°C in $CHCl_3$ chlorooxosilanes are produced. It is particularly useful for converting optically active phosphine oxides $R^1R^2R^3PO$ into the corresponding phosphine. Since the reduction is accompanied by configurational inversion, the intermediacy of a highly nucleophilic $SiCl_3^-$ ion (*cf.* PCl_3) has

[31] O. Graudejus and B. G. Müller, *Z. anorg. allg. Chem.* **1996**, *622*, 1601.
[32] C. Plitzko and G. Meyer, *Z. anorg. allg. Chem.* **1997**, *623*, 1347.
[33] J. Köhler and J.-H. Chang, *Z. anorg. allg. Chem.* **1997**, *623*, 596.
[34] M. Bork and R. Hoppe, *Z. anorg. allg. Chem.* **1996**, *622*, 1557.

been proposed:



The postulation of $SiCl_3^-$ can also accommodate the equally useful, clean, selective reductions by trichlorosilane (bp 33°C) and also the formation of C—C and Si—C bonds by reaction of $SiHCl_3$ with CCl_4, RX, RCOCl, and other halogen compounds in the presence of amines. In these cases the hypothetical $SiCl_3^-$ could be generated by the reaction

$$HSiCl_3 + R_3N \rightleftharpoons R_3NH^+ + SiCl_3^-$$

followed by

$$SiCl_3^- + Cl_3C{-}CCl_3 \longrightarrow SiCl_4 + Cl^- + Cl_2C{=}CCl_2$$

$$SiCl_3^- + RX \longrightarrow [R^- + XSiCl_3] \longrightarrow RSiCl_3 + X^-$$

There is precedent for the postulation of the $SiCl_3^-$ ion, since trisubstituted organosilanes (R_3SiH), react with bases to give silyl ions (R_3Si^-).

Silicon tetrabromide[35] can be prepared by a multi-step procedure by reaction of $C_6H_5SiCl_3$ with $LiAlH_4$ then Br_2 and finally HBr according to:

$$4C_6H_5SiCl_3 + 3LiAlH_4 \xrightarrow[3h/50°C]{Et_2O} 4C_6H_5SiH_3 + 3AlCl_3 + 3LiCl$$

$$C_6H_5SiH_3 + 3Br_2 \xrightarrow[0°C\ to\ 80°C]{CCl_4/N_2} C_6H_5SiBr_3 + 3HBr$$

$$C_6H_5SiBr_3 + HBr \xrightarrow[70°C/5\text{-}6h]{C_6H_6/AlBr_3} SiBr_4 + C_6H_6$$

It can also be prepared from the elements. The fuming liquid is decomposed by water into silicic acid and HBr with great evolution of heat; it reacts violently with potassium.

Chloride Oxides

A variety of chlorooxosilanes, both linear and cyclic, is known. Thus controlled hydrolysis of $SiCl_4$ with moist ether, or interaction of Cl_2 and O_2 on hot silicon, gives $Cl_3SiO(SiOCl_2)_nSiCl_3$, where $n = 1$ to 4.

[35]H.-G. Horn and D. Kuczkowiak, *Z. anorg. allg. Chem.* **1996**, *622*, 1083.

compounds, the Ph groups are equatorial. Six-coordinate $NH_4[Si(NH_3)F_5]$ can be prepared by reaction of silicon powder with NH_4HF_2 in sealed Monel ampoules at 400°C.[62] Several GeF_5^- salts are also known.

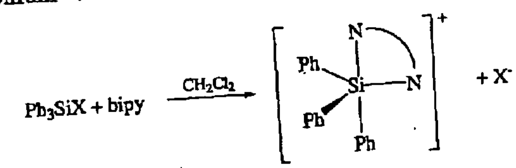
Germanium,[63] tin, and lead also form hexafluoro anions; for example, dissolution of GeO_2 in aqueous HF followed by the addition of KF at 0°C gives crystals of K_2GeF_6. The Ge and Sn anions are hydrolyzed by bases, but most Pb salts are hydrolyzed even by water. Many tin species, $SnF_{6-n}X_n^{2-}$, X = OH^-, Cl^-, Br^-, and so on have been studied by nmr. Anhydrous hexafluorostannates can be made by dry fluorination of the stannates ($M_2^ISnO_3 \cdot 3H_2O$).

The hexachloro ions of Ge and Sn are normally made by the action of HCl or M^ICl on MCl_4. The thermally unstable yellow salts of $PbCl_6^{2-}$ are obtained by the action of HCl and Cl_2 on $PbCl_2$. Under certain conditions, pentachloro complexes of Ge and Sn may be stabilized, for example, by the use of $(C_6H_5)_3C^+$ as the cation or by the interaction of MCl_4 and $Bu_4N^+Cl^-$ in $SOCl_2$ solution.

Other anionic species include the ions $[Ge(SO_3F)_6]^{2-}$ and $[Sn(SO_3F)_5]^-$ formed by oxidation of the element with $S_2O_6F_2$ in HSO_3F, the nitrate $[Sn(NO_3)_6]^{2-}$, and $SnCl_5(THF)^-$.[64] There are also distorted *tbp* spirocyclic oxygen or sulfur chelated anions (e.g., 8-IV and 8-V) that are nonrigid in solution, oxalates $[M(ox)_3]^{2-}$, and other carboxylates.

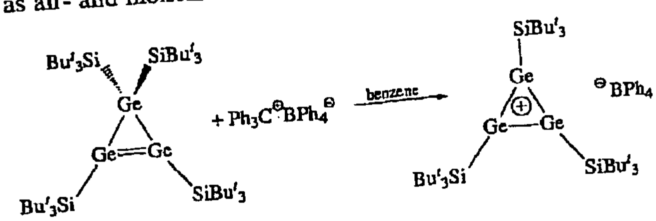
Cationic Species[65]

There are comparatively few cationic complexes, the most important being the octahedral β-diketonates and tropolonates of Si and Ge such as $[Ge(acac)_3]^+$ and Si $trop_3^+$. "Siliconium" ions can also be formed by reactions such as



or by oxidation of $SiCl_2(bipy)_2$ to *cis*-$[SiCl_2(bipy)_2]^{2+}$.

An interesting cyclotrigermenium cation[66] with a 2π system can be isolated in high yield as air- and moisture-sensitive yellow crystals:



[62] C. Plitzko and G. Meyer, *Z. anorg. allg. Chem.* **1996**, *622*, 1646.
[63] J. Stepien-Damm *et al.*, *Z. Kristallogr.* **1996**, *211*, 936.
[64] G. R. Willey *et al.*, *J. Chem. Soc. Dalton Trans.* **1997**, 2677.
[65] R. J. P. Corriu *et al.*, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1097.
[66] P. R. Schleyer, *Science* **1997**, *275*, 39.

$_3$)F$_5$] can be
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The three germanium atoms form an equilateral triangle similar to that of the carbon analogue, the cyclopropenium ion;[67] the cation has Ge—Ge bonds (Section 8-12).

Neutral Species[68]

These are numerous and quite varied in type. Some are 4-coordinate such as SnX_4 and $X_nSn(NR_2)_{4-n}$[69] but the majority are 6-coordinate, examples being *trans*-$SnCl_2(\beta\text{-dike})_2$, $SnCl_2(S_2CNEt_2)_2$, $Sn[(OC_2H_4)_2N(C_2H_4OH)]_2$, and porph SnX_2.[70] Both lower and higher coordination numbers also occur, examples being five in $PhSi(o\text{-}C_6H_4O_2)_2$ and presumably seven or eight in $Sn(S_2CNEt_2)_4$.

Adducts

The tetrahalides are prone to add neutral ligands to form adducts that are usually 6-coordinate. Typical examples are *trans*-$SiF_4(py)_2$, *cis*-$SiF_4(bipy)$, $SiCl_4L_2$ (L = py, PMe_3), and numerous *cis*-SnX_4(L—L) and *cis* or *trans*-SnX_4L_2 compounds.

The Lewis acid order is $SnCl_4 > SnBr_4 > SnI_4$.

8-10 Alkoxides, Carboxylates, and Oxo Salts

All four elements form *alkoxides,* but those of silicon, for example, $Si(OC_2H_5)_4$, often called *silicate esters,* are the most important; the surface of glass or silica can also be alkoxylated. They can be used in the synthesis of ceramic materials.[71] Alkoxides are normally obtained by the standard method:

$$MCl_4 + 4ROH + 4\text{ amine} \longrightarrow M(OR)_4 + 4\text{ amine}\cdot HCl$$

Silicon alkoxides are rapidly hydrolyzed by water, eventually to hydrous silica, but polymeric hydroxo alkoxo intermediates occur. Organo alkoxides such as the *silyl ester* $(MeO)_3SiMe$ and its derivatives are widely known.[72]

Of the *carboxylates, lead tetraacetate* is the most important because it is used in organic chemistry as a strong but selective oxidizing agent.[73] It is made by dissolving Pb_3O_4 in hot glacial acetic acid or by electrolytic oxidation of Pb^{II} in acetic acid. In oxidations the attacking species is generally considered to be $Pb(O_2CMe)_3^+$, which is isoelectronic with the similar oxidant $Tl(O_2CMe)_3$, but this is not always so, and some oxidations are known to be free radical in nature. The trifluoroacetate is a white solid, which will oxidize even heptane to give the CF_3CO_2R species, from which the alcohol ROH is obtained by hydrolysis; benzene similarly gives phenol.

The tetraacetates of Si, Ge, Sn, and Pb also form complex anions such as $[Pb(O_2CMe)_6]^{2-}$ or $[Sn(O_2CMe)_5]^-$. For $M(O_2CMe)_4$, Si and Ge are 4-coordinate

[67] A. Sekiguchi *et al., Science* **1997,** *275,* 60.
[68] C. Y. Wong and J. D. Woollins, *Coord. Chem. Rev.* **1994,** *130,* 175.
[69] See for example: H. Schmidbaur *et al., Chem. Ber./Recueil* **1997,** *130,* 1159; 1167.
[70] D. P. Arnold and J. P. Bartley, *Inorg. Chem.* **1994,** *33,* 1486.
[71] T. J. Boyle and R. W. Schwartz, *Comments Inorg. Chem.* **1994,** *16,* 243.
[72] J. G. Verkade *et al., Inorg. Chem.* **1990,** *29,* 1065.
[73] T. L. Holton and H. Shechter, *J. Org. Chem.* **1995,** *60,* 4725.

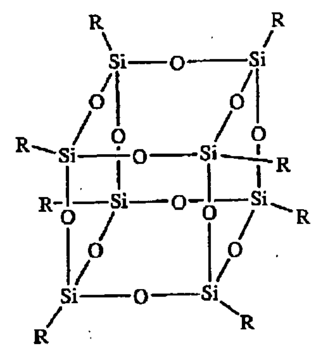
with unidentate acetate; Pb has only bidentate acetates, whereas the smaller Sn has a very distorted dodecahedron.

Tin(IV) sulfate, $Sn(SO_4)_2 \cdot 2H_2O$, can be crystallized from solutions obtained by oxidation of Sn^{II} sulfate; it is extensively hydrolyzed in water.

Tin(IV) nitrate is obtained as a colorless volatile solid by interaction of N_2O_5 and $SnCl_4$; it contains bidentate NO_3^- groups giving dodecahedral coordination. The compound reacts with organic matter.

8-11 Organo Compounds

The general formula is $R_{4-n}EX_n$(n = 0 to 3), where R is alkyl or aryl and X is any of a wide variety of atoms or groups (H, halogen, OR′, NR'_2, SR′, $Mn(CO)_5$, etc.). The elements may also form part of heterocyclic rings or cages,[74] for example $(R_2EO)_3$ or the silsesquioxanes $[RSiO_{3/2}]_n$,[75] such as $R_8Si_8O_{12}$ (8-IX).



(8-IX)

For a given class of compounds, members with C—Si and C—Ge bonds have higher thermal stability and lower reactivity than those with bonds to Sn and Pb. In catenated compounds similarly, Si—Si and Ge—Ge bonds are more stable and less reactive than Sn—Sn and Pb—Pb bonds; for example, Si_2Me_6 is very stable, but Pb_2Me_6 blackens in air and decomposes rapidly in CCl_4, although it is fairly stable in benzene.

The bonds to carbon are usually made *via* interaction of lithium, mercury, or aluminum alkyls or RMgX and the Group 14 halide, but there are many special synthetic methods, some of which are noted later.

Silicon and Germanium

The organo compounds of Si and Ge are very similar in their properties. We discuss only Si compounds.

[74]See for example: P. G. Harrison, *J. Organometal. Chem.* **1997,** *542,* 141 (a review on silicate cages, 221 references).
[75]F. J. Feher *et al., Chem. Commun.* **1997,** 1185.

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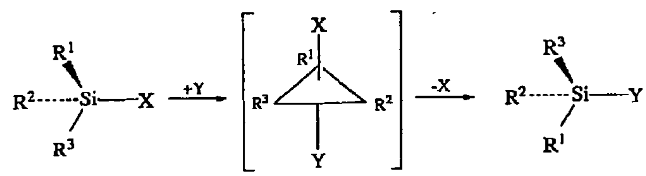
Silicon-carbon bond dissociation energies are less than those of C—C bonds but are still quite high, in the region 250 to 335 kJ mol^{-1}. The tetraalkyls and -aryls are hence thermally quite stable; $Si(C_6H_5)_4$, for example, boils unchanged at 530°C.

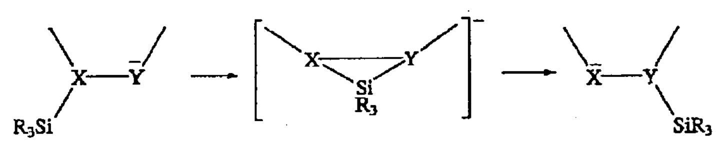
The chemical reactivity of Si—C bonds is generally greater than that of C—C bonds because (a) the greater polarity of the bond $Si^{\delta+}—C^{\delta-}$ allows easier nucleophilic attack on Si and electrophilic attack on C than for C—C compounds, and (b) displacement reactions at silicon are facilitated by its ability to expand the coordination number above 4 by utilization of *d* orbitals.

The reactions of Si compounds have no mechanism analogous to S_N1 reactions at carbon and are generally complicated. Substitution reactions at 4-coordinate silicon characteristically proceed *via* an associative mechanism involving 5-coordinate transition states. Retention or inversion of stereochemistry may occur depending on the nature of the entering or leaving groups, namely,



With the same leaving group, both retention and inversion can be observed; hard nucleophiles tend to attack equatorially to give retention, soft ones apically leading to inversion. Mechanisms depend crucially on the solvent used. If this has donor ability like DMF or DMSO it may attack first to form the 5-coordinate species and is then displaced by an incoming nucleophile.

A characteristic feature of organosilicon (and -germanium) chemistry, setting it strikingly apart from carbon chemistry, is the great ease with which R_3Si (and R_3Ge) groups migrate; a factor of up to 10^{12} as compared to analogous carbon compounds is typical. Among the best studied migration reactions are anionic 1,2-shifts, represented generally by the equation:



where X—Y may be N—N, O—N, or S—C. As indicated, a transition state involving 5-coordinate Si is postulated; since carbon has no valence shell *d* orbitals, it cannot form such a transition state easily, and such 1,2-shifts are "forbidden" in the Woodward-Hoffmann sense.

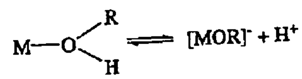
Radicals are less important in silicon than in carbon chemistry. However, silicon radicals have been detected in solution by esr and have been isolated in matrices. They are made by hydrogen abstraction with *t*-butoxy and other radicals generated photochemically, for example,

$$R_3SiH + Me_3CO^{\cdot} \longrightarrow R_3Si^{\cdot} + Me_3COH$$

11-11 Alkoxides and Aryloxides

In solution in alcohols, particularly methanol, metal ions may be solvated just as in water, but the solvent molecules are usually readily displaced by stronger donor ligands such as water itself.

Just as coordinated water can lose a proton (to give hydroxo complexes), so can alcohols:



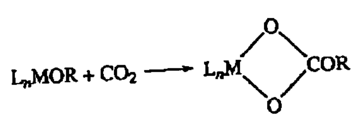
Alkoxide ligands,[82] RO^-, and related oxygen donor ligands such as aryloxides and trialkyl- or triarylsiloxides are hard σ-donors and may also act as π-donors as a result of their filled oxygen $p\pi$-orbitals. They may therefore stabilize metal atoms in relatively high (unusually high) oxidation states, e.g., $Mo(OMe)_6$, and by the selection of appropriate steric properties, they may stabilize metal ions in unusual coordination environments as in $Cr(OBu^t)_4$. As ancillary ligands, the RO σ/π-donation may be adjusted by selection of R. The degree of π-donation is responsive to substrate uptake and release in an analogous manner to say, the slippage of indenyl ligands ($\eta^5 \rightarrow \eta^3 \rightarrow \eta^1$) or the bending of the M—N—O angle of a nitrosyl ligand.

Although M—OR groups are usually bent, in $[ZrCl_4(OMe)(MeOH)]^-$, the ZrOC angle is 171.4°, compatible with a triple bond $Zr \equiv \ddot{O}-Me$.

Alkoxides are known for practically every element of the s, p, d,[83] and f[84] blocks of the Periodic Table and form many heterometallic complexes.[85] They are usually made by reaction of metal halides and alcohols (or phenols) in the presence of a HX acceptor, for example,

$$TiCl_4 + 4EtOH + 4Et_3N \longrightarrow Ti(OEt)_4 + 4Et_3NH^+Cl^-$$

or by use of alkali metal or Tl^I alkoxides. They are normally readily hydrolyzed but thermally stable, distillable liquids or volatile solids. These properties have been used for the preparation of sol-gels for the production of ceramic materials[86] and high purity oxides of the refractory metals by pyrolysis of metal alkoxides. They undergo a wide variety of other reactions such as insertions with small molecules, for example,



[82] M. H. Chisholm, *Chem. Soc. Rev.* **1995**, 79.
[83] W. A. Herrmann *et al.*, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2187.
[84] W. G. Van Der Sluys and A. P. Sattelberger, *Chem. Rev.* **1990**, *90*, 1027.
[85] K. G. Caulton and L. G. Hubert-Pfalzgraf, *Chem. Rev.* **1990**, *90*, 969.
[86] R. C. Mehrotra and A. Singh, *Chem. Soc. Rev.* **1996**, 1.

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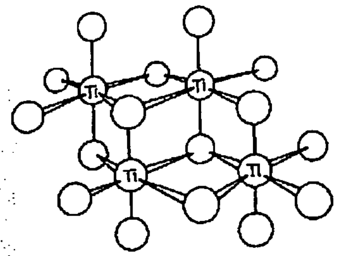


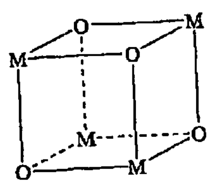
Figure 11-3 The tetranuclear structure of crystalline $[Ti(OC_2H_5)_4]_4$ showing both μ_2 and μ_3 bridges. Only Ti and O atoms are shown. Note that the more bulky trifluoromethyl compound is mononuclear.

and hydrogenolysis, for example,

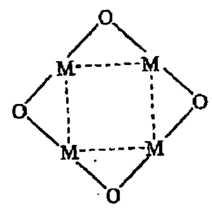
$$(CuOBu^t)_4 \xrightarrow[PR_3]{H_2} (HCuPR_3)_6 + Bu^tOH$$

Nitriles, such as CH_3CN, can produce metathesis reactions with dinuclear alkoxides such $W_2(OBu^t)_6$ to yield $(Bu^tO)_3W{\equiv}N$ and $(Bu^tO)_3W{\equiv}CMe$. In contrast $W_2[OCMe_2(CF_3)]_6$ reacts reversibly to give an adduct, $W_2[OCMe_2(CF_3)]_6(NCMe)_2$.[87]

Most alkoxides with simple groups are polymeric to the extent that maximum coordination of the metal is achieved. Some common types are shown in (11-XII) to (11-XIV) and the structure of another is illustrated in Fig. 11-3.



$(NaOBu^t)_4$
(11-XII)



$(CuOBu^t)_4$
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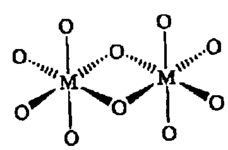


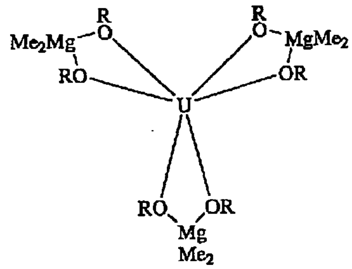
$[Nb(OMe)_5]_2$
(11-XIV)

The use of very bulky alkoxide or aryloxide groups such as $Bu^t_3CO^-$, $Bu^t_3SiO^-$, 2,6-di-*t*-butylphenoxide and adamantoxides can, however, give simple mononuclear species with low coordination numbers.

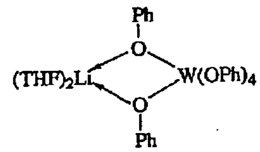
Alkoxo groups not engaged in bridging may, of course act as donors to other metal species. Thus $U(OPr^i)_6$ gives adducts with Li, Mg, and Al alkyls such as

[87] M. H. Chisholm, *J. Chem. Soc., Dalton Trans.* **1996**, 1781.

(11-XV), while in the lithium salt of the $W(OPh)_6^-$ ion, two phenoxides are bound to Li^+ (11-XVI).

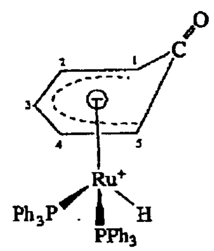


(11-XV)



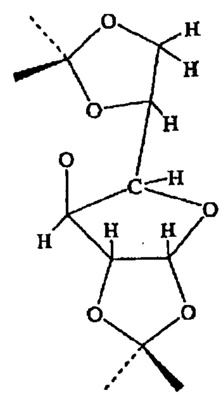
(11-XVI)

Although aryloxides can form unidentate or bridge groups as in $W(OPh)_6$ and $(PhO)Cl_2Ti(\mu\text{-}OPh)_2TiCl_2(OPh)$, respectively, for Ru, Rh and Ir, the phenoxide ion can be bound as a η-1-5-oxocyclohexadienyl (11-XVII) where the C—O group becomes more keto-like and the bonding is delocalized.



(11-XVII)

Chiral alkoxides[88] can be made using sugars, as in MoO_2L_2 and MoO_2L_2(phen), where L is 11-XVIII.



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[88]C. Floriani *et al., J. Chem. Soc., Dalton Trans.* **1995**, 3329; *Prog. Inorg. Chem.* **1997**, *45*, 293; *Chem. Commun.* **1997**, 183.

molecular halides, such as those of B, C, Si, and P. Interhalogen compounds are discussed in the following sections.

Molecular Fluorides

Many molecular fluorides exist, but it is clear that because of the high electronegativity of fluorine, the bonds in such compounds tend to be very polar. Because of the low dissociation energy of F_2 and the relatively high energy of many bonds to F (e.g., C—F, 486; N—F, 272; P—F, 490 kJ mol^{-1}), molecular fluorides are often formed very exothermically; this is just the opposite of the situation with nitrogen, where the great strength of the bond in N_2 makes nitrogen compounds mostly endothermic. Interestingly, in what might be considered a direct confrontation between these two effects, the tendency of fluorine to form exothermic compounds wins. Thus for NF_3 we have

$$\tfrac{1}{2}N_2(g) = N(g) \qquad \Delta H \sim 475 \text{ kJ mol}^{-1}$$

$$\tfrac{3}{2}F_2(g) = 3F(g) \qquad \Delta H \sim 232 \text{ kJ mol}^{-1}$$

$$N(g) + 3F(g) = NF_3(g) \qquad -3E_{N\text{-}F} = -3(272) = -816 \text{ kJ mol}^{-1}$$

Therefore,

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}F_2(g) = NF_3(g) \qquad \Delta H = -109 \text{ kJ mol}^{-1}$$

The high electronegativity of fluorine often has a profound effect on the properties of molecules in which several F atoms occur. Representative are facts such as (a) CF_3CO_2H is a strong acid, (b) $(CF_3)_3N$ and NF_3 have no basicity, and (c) CF_3 derivatives in general are attacked much less readily by electrophilic reagents in anionic substitutions than are CH_3 compounds. The CF_3 group may be considered as a kind of large pseudohalogen with an electronegativity about comparable to that of Cl.

Reactivity

The detailed properties of a given molecular halide depend on the particular elements involved, and these are discussed where appropriate in other chapters. However, a fairly general property of molecular halides is their easy hydrolysis to produce the hydrohalic acid and an acid of the other element. Typical examples are

$$BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3H^+ + 3Cl^-$$

$$PBr_3 + 3H_2O \longrightarrow HPO(OH)_2 + 3H^+ + 3Br^-$$

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4H^+ + 4Cl^-$$

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When the central atom of a molecular halide has its maximum stable coordination number, as in CCl_4 or SF_6, the substance is usually quite unreactive toward water or even OH^-. This does not mean, however, that reaction is thermodynamically unfavorable, but only that it is kinetically inhibited, since there is no room for nucleophilic attack. Thus for CF_4 the equilibrium constant for the reaction

$$CF_4(g) + 2H_2O(l) = CO_2(g) + 4HF(g)$$

is $\sim10^{23}$. The necessity for a means of attack is well illustrated by the failure of SF_6 to be hydrolyzed, whereas SeF_6 and TeF_6 are hydrolyzed at 25°C through expansion of the coordination sphere, which is not possible for sulfur.

Organic Halides as Ligands

There is an extensive chemistry of organic halides as ligands[20] that includes now R_3SiX.[21] The compounds can be obtained by reactions such as

$$L_nMCl + AgPF_6 + RI \xrightarrow[-AgCl]{CH_2Cl_2} [L_nM \leftarrow IR]^+PF_6^-$$

$$L_nRuI + CF_3SO_3Me \longrightarrow [L_nRu \leftarrow IMe]^+CF_3SO_3^-$$

$$Cp(NO)(Ph_3P)ReCH_3 \xrightarrow[+CH_2Cl_2,\ -CH_4]{HBF_4\cdot OEt_2} [Cp(NO)ReClCH_2Cl]^+BF_4^- \xrightarrow{RI} [Cp(NO)ReIR]^+BF_4^-$$

Although the compounds are mainly of the angular type M···XR, there are numerous examples of compounds with bridging or chelate groups arising from halides such as CH_2I_2, $Cl(CH_2)_2Cl$, $I(CH_2)_3I$, and so on. An example is $[Ir^{III}H_2(PPh_3)_2(\eta^2\text{-}1,2\text{-}C_6H_4I_2)]^+SbF_6^-$. Silver complexes have been particularly well studied.[22] A different type of complex has an $M\cdots X-CH_2-M$ unit with an M—C bond;[23] aryl fluorides have also been shown to coordinate to $RuCl_2(PPh_3)_3$.[24] Compounds with organic halide ligands can be useful starting materials as the halides can often be easily replaced by other ligands.

[20] R. J. Kulawiec and R. H. Crabtree, *Coord. Chem. Rev.* **1990**, *99*, 89.
[21] R. U. Kirss, *Inorg. Chem.* **1992**, *31*, 3451.
[22] J. Powell *et al., J. Chem. Soc., Dalton Trans.* **1996**, 1669; R. D. Gillard *et al., Polyhedron* **1996**, *15*, 2409.
[23] Y. Zhou and J. A. Gladysz, *Organometallics* **1993**, *12*, 1073.
[24] S. D. Perera and B. L. Shaw, *Inorg. Chim. Acta* **1995**, *228*, 127.